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The effect of small additions of co on the density and surface properties of liquid tin

Introduction

Tin is one of the most important low melting point metals which, due to its physical and chemical properties, are widely used in various fields of industry. Besides the classic applications as a basic component of solders, fuses, etc., it was also important to micro- and nanoelectronics and other high-tech industries. However, the effective use of tin-based alloys requires knowledge on structure and physical properties, as well as their change with adding other elements. Particularly, it is interesting both from fundamental and applied viewpoints to study the alloys of tin to which a ferromagnetic elements are added.

The paper presents the results of the influence of small additions of such ferromagnetic element as cobalt on the density and surface tension of liquid tin. It is known that in many cases a small amount of the added element significantly changes the surface tension of different kinds of liquids, including metallic melts. Unfortunately, there are no literature data on the influence of small amount of ferromagnetic elements additions on surface tension of liquid metals. From the structure studies results of Co-Sn system in liquid state by means of X-ray diffraction method it follows that atomic distribution in liquid alloys of this system is significantly different from the atomic solution and atoms attempt to form clusters, the chemical composition of which depends on the content of cobalt and temperature (Yakymovych, Shtablavyi, Mudry 2014; Mudry, Komarnytsky, Korolyshyn, Prokhorenko 1995; Mudry, Komarnytsky, Halchak, Korolyshyn 1993; Komarnytsky, Mudry, Halchak 1998; Mudry, Prokhorenko, Prokhorenko, Bojar 2006; Kazimirov, Roik, Sokolskii 2010). Interest in studying the melt of this system has increased in recent years, both due to the physics of metal melts and in practical terms.

Sessile drop method measured the density and the surface tension of liquid tin melts containing 2.5; 5 and 10 atm. % Co at different temperatures.

Results and discussion

Results of structural studies of molten alloys of system Co-Sn (Komarnytsky, Mudry, Halchak 1998) have shown that these elements do not form the random atomic distribution and exhibit a tendency to preferred interaction of unlike kind atoms. Analyzing the temperature dependence of structural parameters, we have seen that these parameters are much more sensitive to temperature than the simple models of metallic melts predict. This fact allowed for an assumption that the simple topological disordering of structure increasing with temperature is accompanied also by significant changes in short-range order.

Taking into account the negative value of enthalpy of mixing (Ivanov 1991; Cömert, Pratt 1985), as well as other features of the physical and chemical properties (viscosity, resistivity, density, etc.) (Yakymovych, Plevachuk, Mudry, Brillo, Kobatake, Ipser 2014; Xu, Wang, Wei 2004; Hitara, Waseda, Jain, Srivastava 1977), we can assume that these molten alloys consist of elementary structural units (clusters)

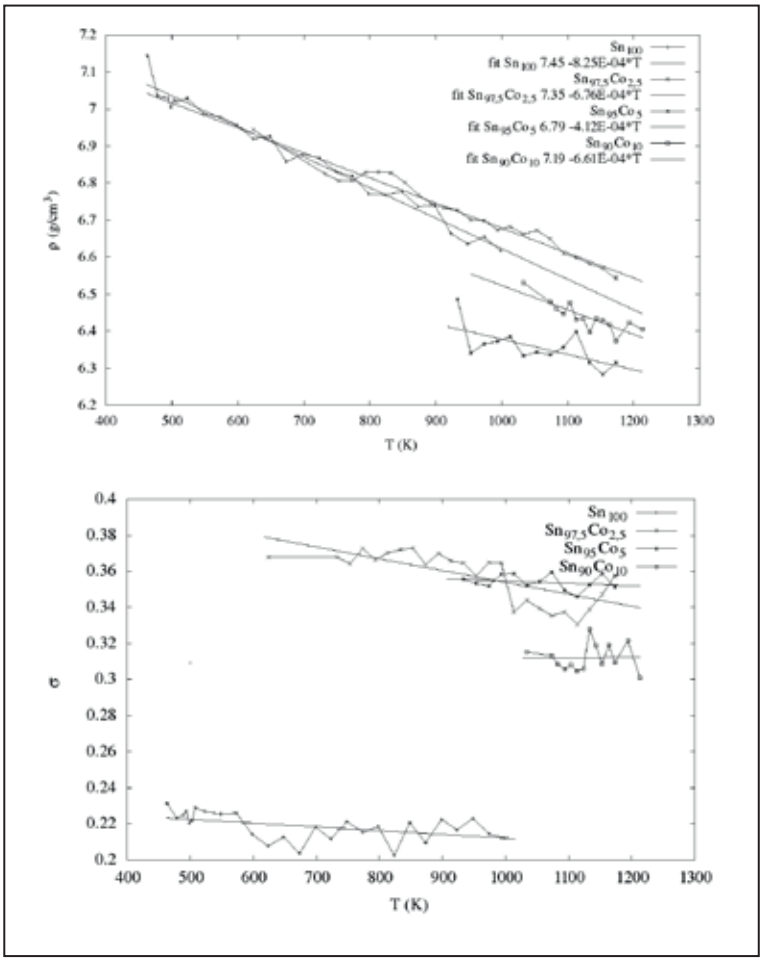

Fig. 1. Temperature dependence of the density (a) and surface tension (b) of molten Sn-Co alloys

which reveal the chemical short-range order close to the structure of intermetallic phases existing in phase diagram of this binary system. It is clear that the ratio between the atoms forming such clusters is a certain value and not necessarily the same as for the corresponding crystalline phases. Thus, we can assume the existence of stoichiometric clusters which particularly affect the temperature and concentration dependence of the structure and properties. These clusters are not separate phases or dynamic atomic groups with a certain number of atoms; their study is difficult compared with stable clusters and nanoparticles. It is important that these clusters interact with individual atoms. To separate cluster-cluster and cluster-atomic structures using the common structural characteristics is also not an easy task and requires more information on the nanoscale level, including data on small-angle diffraction.

Notably those components of the Co-Sn significantly differ in their main physical and chemical characteristics that are pronounced in phase diagram, in which no solid solution concentration regions. In liquid state their structural parameters are

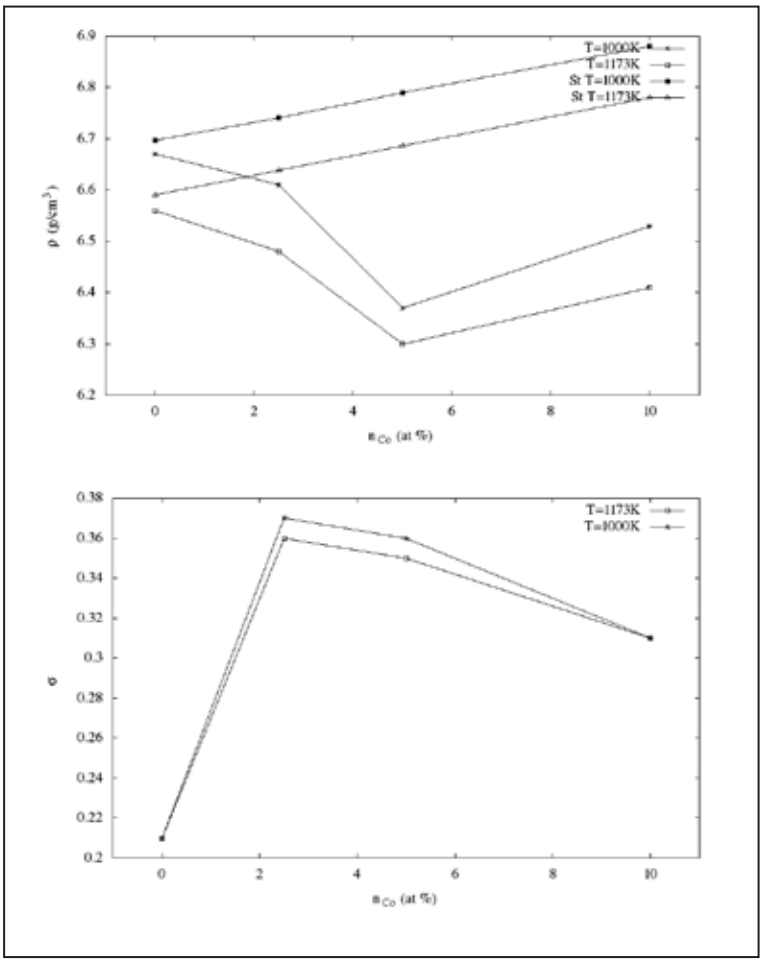

Fig. 2. Concentration dependence of density (a) and surface tension (b) of molten Sn-Co alloys

also significantly different, which is a reason of inhomogeneous structure observed in experimental studies of the structure by means of X-ray diffraction method. This includes physical characteristics such as density and surface tension. The first one describes the volume properties of the melt, and the second – the surface properties, although both can be obtained through the experimental method.

The temperature dependence of the density of liquid tin melt containing 2.5 atm % Co is close to such dependence of liquid tin (Fig. 1 a), and the discrepancy between them is greater at higher temperatures and it is the evidence that at higher temperatures Co atoms effectively influence the atomic distribution of liquid tin. It is likely that at low temperatures a significant amount of tin atoms form clusters Sn_n and individual atoms. Occupying intercluster pores they try to stay there and thus increase the density of the melt, i.e. in this case cobalt promotes atomic packing density compared with pure tin. With increasing Co content up to 5 atm % the density value starts to decrease, as well as its temperature coefficient.

Concentration dependencies of density are shown in Fig. 2(a), where they are compared with additive dependences for two temperatures. One can see that addition of cobalt atoms to tin significantly reduces the density, which is much different from the typical values for statistical atomic distribution. This decrease in density can be explained by the fact that the atoms of cobalt try to form chemically ordered clusters of tin atoms, and because the intermetallics in Co-Sn system have lower density of atomic packing (which can be also lower in clusters) and density of melt will decrease despite this fact, the density of pure cobalt is greater than the density of tin. However, with further addition of Co density begins to grow, trying to approach the values characteristic of the atomic solution. It begins to show a stronger tendency to interaction of unlike kind atoms. Thus, we can assume that the formation of clusters of chemically ordered atoms reduces the density of atomic packing, which in turn leads to variation in the concentration dependence of density.

Experimental values of the surface tension at different concentrations also reveal different temperature coefficient, which indicates that the addition of cobalt does not lead to the formation of random atomic distribution in the surface layers of the melt as well. If we analyze the dependence of the surface tension on cobalt content the behavior is found to be abnormal. With increasing concentration of cobalt the surface tension increases, the most likely reason being that the Co atoms at the surface are very active, perhaps more active than in the bulk. Moreover, taking into account the cluster structure of liquid tin, it is quite possible that in this case the formation of the surface layer the contribution to atom-cluster interaction Sn_n-Co is significant. With further increase of 3d-element content the surface tension is reduced slightly, due to some rearrangement of atoms in the surface layer that has caused the attempt of cobalt atoms to create chemically ordered clusters with tin atoms Co_mSn_n.

It should be noted that a temperature increase of $\Delta T = 173K$ does not lead to significant changes and the behavior of concentration dependence displays the changes in cluster-cluster and atom-cluster structures of the surface layer. The results of investigation allowed us to assume that cluster temperature stability is high.

Thus, from the results of measuring the density and the surface tension follows that tendency to preferred interaction of unlike kind atoms in molten Sn- enriched

Sn-Co alloys exists both in the bulk of melt and in its surface layer and it leads to the formation of chemically ordered clusters.

Conclusion

Addition of Co (2.5; 5 and 10 atm %) to tin leads to abnormal changes in the density and the surface tension in comparison with hypothetical atomic solution. The observed changes in these physical parameters can be explained by the formation of clusters of atoms of cobalt and tin both in the bulk of melt and in its surface layer. These chemically ordered clusters are stable within certain temperature range and can be transformed by changing the component concentration in alloy.

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Abstract

Density and surface tension of the molten Sn-Co containing 2.5; 5 and 10 at% of Co have been studied by means of sessile drop method. The temperature dependence of obtained parameters is analyzed and interpreted from the viewpoint of cluster structure. It is shown that the density and the surface tension reveal an anomalous behavior due to the formation of chemically ordered clusters on the surface and in the bulk melt.

Key words: metallic alloys, tin-nickel, surface tension, clusters.

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